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A. Göller, U.-W. Grummt

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Implementation of an NDDO/CI/SOS Approach for Second-Order Hyperpolarizabilities

Andreas Göller, Ulrich-Walter Grummt*
Institut für Physikalische Chemie, Friedrich-Schiller-Universität Jena,
Lessingstraße 10, 07743 Jena, Deutschland
goeller@pc04.chemie.uni-jena.de

The sum-over-states (SOS) formalism implemented in VAMP [1] for NDDO-Hamiltonians AM1, PM3 and MNDO for the calculation of hyperpolarizabilities [2a, 2b] was extented to third-order nonlinear optical properties [2c] and its application to third harmonic generation (THG). Extensive comparisons between THG experimental data and published MOPAC/FF to VAMP/PECI/SOS and AMPAC/FF calculated values were carried out in gas phase and in solvent for a data set of 236 compounds of the general type DπA and conjugated π-systems. Great care was taken to derive the global minimum conformers yielding significant deviations of the geometries derived by the three Hamiltonians. The data set therefore gives an overview of the shortcomings and strengthenesses of the semiempirical methods. Here, the implementations of solvent effects in both semiempirical packages especially are problematic in the case of elongated molecules, so a threshold for molecular globularity had to be defined to eliminate erroneous data. The presented correlation statistics for γ are in acceptable agreement for the whole data set as for all experimentally well-defined substance classes with scalable correlation slopes smaller than unity. The data become more reliable for large γ, probably due to more precise experimental values. Inclusion of solvent effects raises the polarizabilities of the molecules consistently. These results enable us to qualitatively predict trends for small as well as large second-order polarizabilities, derive scaling functions for quantitative predictions and calculate tensor elements of γ experimentally not accessible. The SOS formalism even allows us to obtain insights in frequency-dependence of second-order hyperpolarizability effects beyond THG.

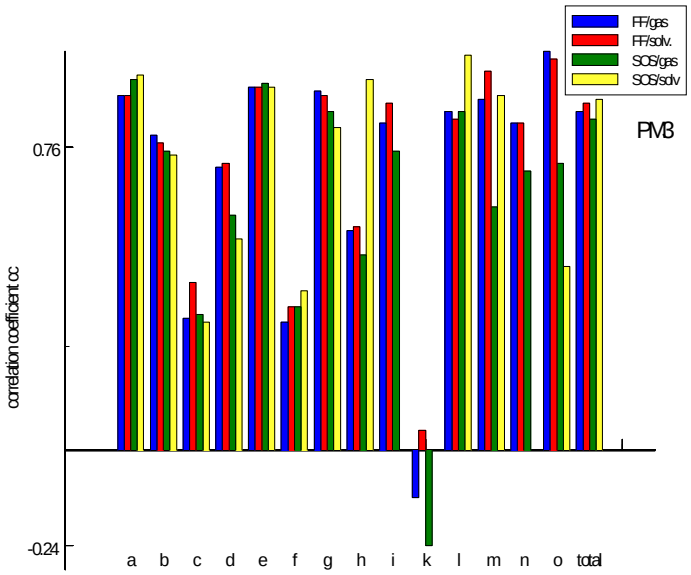

Figure 1: Experiment *vs.* calculation correlations for gas phase and solvent model derived <γ> with AMPAC/finite field and VAMP/CI/SOS methods for the different substance classes

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